Tetrahedron Letters No. 10, pp. 449-452, 1962. Pergamon Press Ltd. Printed in Great Britain.

DEHALOGENATION OF HALOGENOBICYCLO-[2.2.1]-HEPTANE DERIVATIVES - I

NEW ROUTES TO BENZNORBORNENE AND RELATED COMPOUNDS

Peter Bruck

Chemistry Department, The University, Hull

(Received 16 April 1962)

THE total dechlorination of the insecticide isodrin (Ia) and related compounds by means of lithium and t-butanol proceeds readily in refluxing tetrahydrofuran solvent,[1] the geminal, allylic and even the bridgehead chlorine atoms being replaced by hydrogen with ease. The reaction provides a good synthetic route to several systems containing fused bicycloheptane rings,[1-3] which are only difficultly accessible by other means.[4] From isodrin itself, the major product is the endo-endo[5] diene (Ib), which can be isolated by preparative vapour phase chromatography.

In the present work, substantial amounts of benznorbornene[6] (IIc) and benznorbornadiene[6] (IIIb) were required, in connexion with another study. These compounds, and derivatives thereof,[7] are accessible by means of the elegant procedure of Wittig and Knauss,[8] which involves the addition of

---

[1] P. Bruck, D. Thompson and S. Winstein, Chem. & Ind. 405 (1960).

[2] S. Winstein and R.L. Hansen, J. Amer. Chem. Soc. 82, 6206 (1960).

[3] P. Bruck and D. Thompson, unpublished work, University of California, Los Angeles, 1958-1960.

[4] L. DeVries and S. Winstein, J. Amer. Chem. Soc. 82, 5363 (1960).

[5] For the question of nomenclature of fused bicycloheptane systems see
a S.B. Soloway, J. Amer. Chem. Soc. 74, 1027, footnote 7 (1952);
b J.K. Stille and D.A. Frey, Ibid. 81, 4273 (1959).

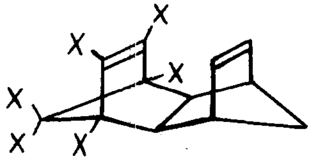
[6] The nomenclature and numbering proposed by J. Meinwald and G.A. Wiley, J. Amer. Chem. Soc. 80, 3667 (1958) has been followed; see also ref. 7.

[7] P.D. Bartlett and W.P. Giddings, J. Amer. Chem. Soc. 82, 1240 (1960).

[8] G. Wittig and E. Knauss, Chem. Ber. 91, 895 (1958).

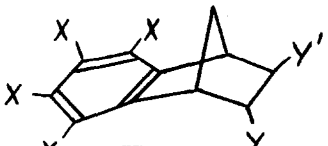
benzyne to cyclopentadiene; however, on the substantial scale, this route is somewhat expensive due to relatively high costs (in some countries) of the requisite starting materials for the preparation of benzyne. Mackenzie[9] has reported the preparation of some polyhalogeno benznorbornenes, derived initially from the Diels-Alder adduct of 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene with norbornadiene; among these were 3',4',5',6'-tetrachlorobenznorbornene[6] (IIa), 2,3-dibromo-3',4',5',6'-tetrachlorobenznorbornene[6] (IIb) and 3',4',5',6'-tetrachlorobenznorbornadiene[6] (IIIa). We have now treated these compounds with lithium and t-butanol in tetrahydrofuran (THF), in the hope that dehalogenation would provide alternative routes to benznorbornene derivatives.

Treatment of IIa or IIb with cut lithium ribbon (3 g atom per halogen; 50 per cent excess) and t-butanol (2 molar equiv. per halogen; 100 per cent excess) in THF under an inert atmosphere resulted in smooth vigorous dehalogenation reactions from which were obtained 94 and 87 per cent yields respectively of benznorbornene (IIc), b.p. 80-82°/10 mm (Found: C, 91.7;



I

a, X = Cl; b, X = H



II

a, X = Cl, Y = Y' = H

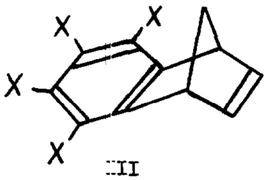
b, X = Cl, Y = Y' = Br

c, X = Y = Y' = H

d, X = Cl, Y = H, Y' = O.COCH$_3$

e, X = Cl, Y = H, Y' = OH

f, X = Y = H, Y' = OH



III

a, X = Cl; b, X = H

---

[9] K. Mackenzie, *J. Chem. Soc.* 473 (1960).

H, 8.2%. Calc. for $C_{11}H_{12}$: C, 91.6; H, 8.4%). The product was homogeneous on vapour phase chromatography,[10] and was identical with the product obtained from a sample of benznorbornadiene, prepared by the method of Wittig and Knauss,[8] by hydrogenation over platinum on charcoal. Proceeding batchwise (20 g batches), IIa (160 g) could be converted to IIc (76 g) in ca. 5 hr.

Treatment of IIIa with lithium (2.3 g atom per halogen; 15 per cent excess) and t-butanol (1.3 molar equiv. per halogen; 30 per cent excess) in refluxing THF gave a 79 per cent yield of a liquid mixture, b.p. 86-90°/15 mm, which took up 0.81 moles of hydrogen over platinum on charcoal. On examination by vapour phase chromatography,[10] the mixture was found to contain benznorbornene (IIc) and benznorbornadiene (IIIb) in a ratio of 18:82[11] (Found: C, 92.61; H, 7.37%. 18% IIc, 82% IIIb requires C, 92.67; H, 7.33%). IIIb could be separated from the mixture by means of its silver nitrate complex,[12] from which it could be regenerated by ammonia solution or dilute nitric acid. The purified material had b.p. 87-88°/15 mm and was homogeneous on vapour phase chromatography.[10] The infra-red spectrum was identical with that of authentic material.

Treatment of IIIa with refluxing acetic acid containing a catalytic amount of sulphuric acid[7,13] gave a 76 per cent yield of exo-2-acetoxy-3',4',5',6'-tetrachlorobenznorbornene (IId), m.p. 137-138° (uncorr.) (Found: C, 46.4; H, 2.85; Cl, 41.7%. Calc. for $C_{13}H_{10}Cl_4O_2$: C, 45.9; H, 2.96; Cl, 41.7%). Hydrolysis of IId with potassium hydroxide in aqueous

---

[10] Pye Argon instrument, 10 per cent Apiezon L on Celite, 100°.

[11] When larger excesses of lithium were used, the percentage of the over-reduced material IIc in the final product increased markedly, being 76 per cent of the whole when 4 g atoms of lithium (100 per cent excess) were used per halogen atom.

[12] S. Winstein and H.J. Lucas, J. Amer. Chem. Soc. 60, 836 (1938).

[13] J. Bertram and H. Walbaum, J. Prakt. Chem., N.F. 49, 1 (1894).

methanol gave the corresponding alcohol, exo-3',4',5',6'-tetrachlorobenznorbornen-2-ol, (IIe), m.p. 123-124° (uncorr.) (Found: C, 44.1; H, 2.26; Cl, 47.0%. Calc. for $C_{11}H_8Cl_4O$: C, 44.3; H, 2.71; Cl, 47.6%).

Treatment of IIe with lithium (3 g atom per halogen) and t-butanol (2 molar equiv. per halogen) in THF gave a 65 per cent yield, after chromatography on alumina with ether, of exo-benznorbornen-2-ol (IIf), m.p. 74.5-75.5° (Found: C, 82.2; H, 7.56%. $C_{11}H_{12}O$ requires C, 82.5; H, 7.53%), identical in all respects with material prepared from IIIb, either by the method of Bartlett and Giddings[7] or by the hydroboration-oxidation method of Brown and co-workers.[14]

A study of the rates of solvolysis of sulfonate esters of the tetrachloro-alcohol (IIe) is of interest in connexion with the solvolysis of the brosylate of the related alcohol (IIf)[7] and of derivatives of exo-norborn-5-en-2-ol.[15] Such work is proceeding at the present time.

This work was carried out during the tenure of an I.C.I. Research Fellowship; the awarding of this by the University of Hull is acknowledged. Thanks are also due to Shell Research, London and Shell Pernis, Rotterdam, for a gift of chemicals.

---

[14] H.C. Brown, K.J. Murray, L.J. Murray, J.A. Snover and G. Zweifel, J. Amer. Chem. Soc. 82, 4233 (1960) and previous references therein.

[15] S. Winstein and M. Shatavsky, J. Amer. Chem. Soc. 78, 592 (1956).